

Molecular Simulations of Shock to Detonation Transition in Nitromethane

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An extension of the model described in a previous work of Maillet, Soulard and Stoltz [1] based on a Dissipative Particle Dynamics is presented and applied to liquid nitromethane. Large scale non-equilibrium simulations of reacting nitromethane under sustained shock conditions allow a better understanding of the shock-to-detonation transition in homogeneous explosives. Moreover, the propagation of the reactive wave appears discontinuous since ignition points in the shocked material can be activated by the compressive waves emitted from the onset of chemical reactions.

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Since two decades, molecular dynamics (MD) has become a widely used numerical tool to model and understand shock waves processes. It has been successfully used to study the appearance of plasticity and phase transition under shock conditions [2, 3], as well as the structure of the shock front [4]. Similar successes have not been obtained in the study of high energetic materials, in particular for the formation of a reactive (detonating) wave. This is mainly due to the very large time and length scales required to observe such phenomena. Simulations of reactive waves have been limited so far to model materials, mainly using the REBO potential or some of its variants [5, 6]. For real energetic materials, only the first steps of the decomposition mechanism of RDX under shock conditions were studied using reactive classical MD [7]. The same model allowed the simulation of the onset of the reactive wave [8]. Finally, modified equations of motion (*i.e.* constrained dynamics) allowed to model shock properties of reacting systems [9], but the behavior of the wave itself is not accessible. In conclusion, full atomistic simulations of detonations in realistic explosives have never been achieved so far since the involved computational burden outperforms all current computer resources by orders of magnitude.

Having in mind that detonation ultimately is a multi-scale process coupling hydrodynamical features and local chemical reactions, coarse graining strategies appear as a relevant alternative to a full direct numerical simulation of the entire detonation process. The coarse-graining approach was only recently considered for shock waves [10–12]. It is based on the replacement of complex molecules by mesoparticles with internal degrees of freedom.

In this letter, we present equations of motions for mesoparticles including energy exchange between intramolecular and intermolecular degrees of freedom in order to ensure energy conservation, DPDE (standing for 'Dissipative Particle Dynamics at constant Energy'). Moreover, additional variables are added to each particle

to account for its possible chemical evolution. The dynamics of these variables is governed by classical kinetic equations. The final model, RDPDE (standing for 'Reactive DPDE'), is used to study the shock to detonation transition mechanism in nitromethane.

Description of the model. We first briefly recall the DPDE model used to simulate inert shock waves in [12]. For a system of N particles q_i with momenta $p_i = m_i v_i$, the equations of motion read

$$\begin{aligned} dq_i &= \frac{p_i}{m_i} dt, \\ dp_i &= -\nabla_{q_i} V(q) dt - \gamma_{ij} \chi^2(r_{ij}) v_{ij} dt + \sigma \chi(r_{ij}) dW_{ij}, \\ d\varepsilon_i &= \frac{1}{2} \sum_{j, j \neq i} \chi^2(r_{ij}) \left(\gamma_{ij} v_{ij}^2 - \frac{3\sigma^2}{2} \left(\frac{1}{m_i} + \frac{1}{m_j} \right) \right) dt \\ &\quad - \sigma \chi(r_{ij}) v_{ij} \cdot dW_{ij}, \end{aligned} \quad (1)$$

where $V(q)$ is the interaction potential between mesoparticles (a sum of pairwise interactions here), $r_{ij} = |q_i - q_j|$ and $v_{ij} = \frac{p_i}{m_i} - \frac{p_j}{m_j}$ are respectively the distance and the relative velocity between particles i and j , $\chi(r)$ is a weighting function with cut-off radius r_{cut} , and the processes W_{ij} are independent d -dimensional Brownian motions with $W_{ij} = -W_{ji}$. The following fluctuation-dissipation relating the magnitude of the stochastic forces σ to that of the friction forces $\gamma_{ij} > 0$ ensures that the canonical distribution is invariant: $\gamma_{ij} = \frac{\sigma^2 \beta_{ij}}{2}$, $\beta_{ij} = \frac{1}{2k_B} \left(\frac{1}{T_i} + \frac{1}{T_j} \right)$. In the latter equation, the temperatures T_i are internal temperatures obtained from an internal equation of state (EOS) on the internal energy: $\varepsilon_i = \int_0^{T_i} C_{v_i}(T) dT$. The explicit temperature dependence of the function C_{v_i} allows to accurately reproduce the thermodynamic behavior of the internal degrees of freedom (DoFs). As discussed in [13], this function is known to modify the response of materials to shock loading. For reactive material, or in the more general case

when some processes are activated by the temperature of internal DoFs, this function is expected to play an important role as well.

For reactive materials, additional variables per particle λ_i are introduced to model the progress of the chemical reactions at hand [1]. Their time evolution equations depend on the order of the chemical reactions and the reversible natures of the latter. We have chosen to model the chemical decomposition of nitromethane with a succession of two first order chemical reactions: The first one is reversible and endothermic, while the second one is irreversible and exothermic. One mesoparticle could represent successively all states between NiMe and products. The model reaction of the decomposition of nitromethane is:



where NiMe^* represents a metastable material corresponding to a local minimum on the potential energy surface. The progress variables λ_1 and λ_2 represent the evolutions of the two chemical reactions, and can be identified with the fractions of NiMe^* and Products respectively. Their time evolution reads:

$$\frac{d\lambda_1}{dt} = k_1(1 - \lambda_1 - \lambda_2) - k_{-1}\lambda_1 - k_2\lambda_1, \quad (2)$$

$$\frac{d\lambda_2}{dt} = k_2\lambda_1, \quad (3)$$

where k_1 and k_{-1} are the forward and backward reaction rates associated to the first chemical reaction and k_2 is the reaction rate associated to the second chemical reaction. The expressions of these rates are given by standard Arrhenius expressions : $k = A \exp(-E_a/RT)$ where E_a is the activation energy and T is obtained from a local spacial average of internal temperatures.

The model is constructed so that the total energy of the system (the sum of the potential, kinetic, internal and chemical energies) is constant. In particular, the energy variations due to chemical reactions are compensated by appropriate variations of the kinetic and internal energies, as described in [1].

Application to nitromethane. The interactions between mesoparticles are described by a classical exp-6 potential, which is known to ensure a good compressibility of the system at high pressure. By means of the analytical expression of the equation of state of exp-6 fluids proposed by Kataoka [14], the parameters of the potential for inert nitromethane and its detonation products are obtained respectively by optimization on experimental Hugoniot [15–17] and Crussard curves [18]. Consistency of these potentials with experimental data is shown on Figure 1. From now on, computations are made with these potentials. When a DPD particle is reacting ($0 < \lambda_i < 1$), the parameters of the interaction potential are given by a linear interpolation of the param-

eters of the potential for the inert and the fully reacted system.

For inert nitromethane, as the DPD particle represents only a single nitromethane molecule, there is a clear splitting between internal and external DoFs: the internal C_v of the DPD particle represents simply the sum of the intramolecular contributions to the energy. Hence the C_v function is taken directly from thermodynamic tables. For the fully reacted material, a DPD particle represents the decomposition products of one nitromethane molecule, *i.e.* a group of several small molecules. The corresponding internal C_v is then a sum of two contributions: the internal DoFs of the small molecules plus a fraction of their external DoFs. There is no clear splitting between intra and intermolecular DoFs in the coarse graining process. Therefore, the C_v function of the DPD particle cannot be extracted from a standard thermodynamic table, and has to be computed numerically as the difference between the total C_v of the real system and the C_v due to the intermolecular DPD potential only. In the following internal DoFs will stands for all DoFs inside a mesoparticle and external DoFs will stands for displacement of mesoparticles.

The rate of heat exchanges between internal and external DoFs is controlled by the parameter σ . Dawes *et al* [19] have presented a study of energy relaxation in solid nitromethane behind a shock wave. They computed the rate of energy transfer between translational and rotational kinetic energies and internal vibrational modes. Of course, some of the vibrational modes that exhibit an efficient coupling to the phonons are therefore heated rapidly after the shock, while some other modes heat up more slowly. In the DPD model we use, there is only one mode representing the average of all internal vibrations. We chose a value of σ leading to an equilibration time of a few picoseconds between intra and intermolecular DoFs.

Numerical results. All simulations have been performed with our in-house parallel MD code. We used a time step $\Delta t = 1$ fs in our simulations, a value at least one order of magnitude larger than for MD simulations with standard reactive potentials as such ReaxFF.

The thermodynamic properties of our model have been studied by equilibrium and nonequilibrium MD simulations. The computed density of the material at $P = 1$ bar and $T = 300$ K is 1.1041 g.cm^{-3} . Simulations of inert nitromethane using the hugoniot constraint method and NEMD (shock simulations) have been performed in order to compute the inert Hugoniot curve. Similar simulations are performed with reacted nitromethane to compute the Hugoniot curve of detonation products, *i.e.* the Crussard curve. Results are displayed in Figure 1. A semi-quantitative agreement is found on thermodynamical properties of both the inert and reacted explosive.

Nonequilibrium shock wave simulations have been performed with the RDPDE model. Sustained shock simulations have been loaded on sample of size $20 \times 20 \times 10000$

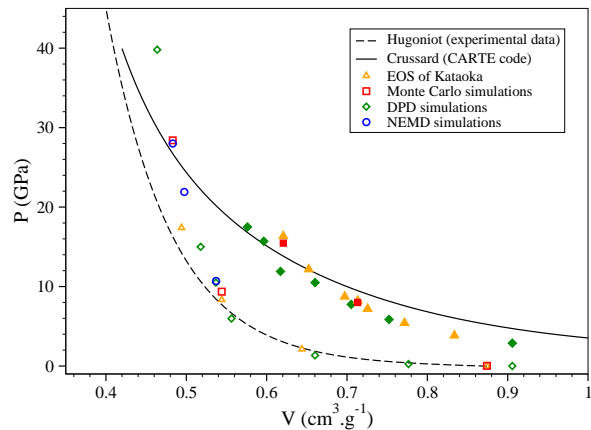


FIG. 1: Hugoniot and Crussard curves of nitromethane. Black line: experimental Hugoniot curve. Dotted line: Crussard curve (CARTE code). Open symbols correspond to inert nitromethane while full symbols correspond to detonation products. Triangles: calculations made with the EOS of Kataoka. Squares: Monte Carlo simulations. Diamonds: MD-DPD equilibrium simulations. Circles: non equilibrium shock simulations.

unit cells (about $4.5\mu\text{m}$ long), with an infinitely massive piston moving at constant velocities equal to 1500, 2000, 2500, 2700 and 3000 m.s^{-1} . The total simulation time for each simulation is around 700 ps. In the simulations with piston velocities equal to 1500 and 2000 m.s^{-1} , no sign of reactive wave formation is observed. The inert shock wave propagates through the whole sample, activating the explosive with the first reversible reaction, but the detonation products are not produced. This is due to the fact that the shock did not release enough energy for the system to overcome the energy barrier of the second (irreversible) reaction. For piston velocities equal to or higher than 2500 m.s^{-1} , we observe the decomposition of the explosive and the formation of a reactive wave. The velocity of the corresponding wave now exceeds the one of the inert shock wave due to the global energy release of exothermic reactions.

On the experimental side, multiple-magnetic gauge measurements of neat nitromethane [20] allowed the direct observation of the shock-to-detonation mechanism: A reactive wave first builds up in the shocked (inert) material (characterized by an increase of the particle velocity as the wave propagates) and forms a superdetonation wave travelling at constant velocity. This superdetonation wave overtakes the inert shock wave and progressively decays to an overdriven, and eventually to a steady, detonation. This has recently been confirmed by PDV (Photonic Doppler Velocimetry) measurements [21].

For the simulation using a piston velocity of 2700 m.s^{-1} , the onset of the reactive wave is evidenced in Figure 2 by the signal of (artificial) multiple gauges. This wave progressively catches up with the shock wave. These signals exhibit striking similarities

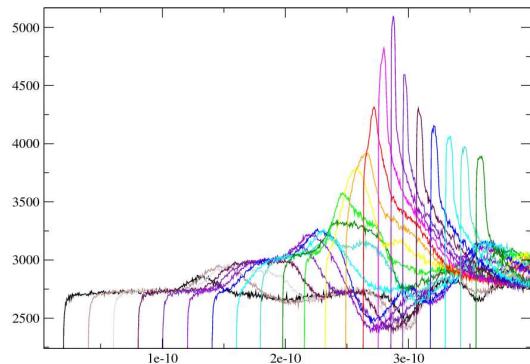


FIG. 2: Time evolutions of particle velocities taken at different locations in the material (every 50 cells), mimicking the behaviour of multiple gauges set up.

with experimental measurements, although occurring on a shorter timescale. The complete scenario of the shock-to-detonation transition is displayed in Figure 3, which shows the evolutions of the average velocity, progress variable, internal temperature and the x -component of the pressure tensor, in a (x, t) diagram.

After a shock wave is loaded in the sample it leaves the nitromethane in an shocked state. After around 100 ps, chemical reactions start to occur at the interface with the piston since this is the region of space where the system has spent the longest time in the shocked state. As the chemical reactions progress, a reactive wave is formed, which travels in the shocked nitromethane at a higher velocity than the shock wave. Its front is given by the analysis of the diagram of the progress variable. From the onset of chemical reactions happening around 100 ps, a compressive wave is created, travelling much faster than the reactive wave in the shocked material, up to the inert shock front. This compressive wave brings the inert shocked system at a slightly higher density. When it reaches the shock front, it accelerates and increases the pressure (and the material velocity) in the shocked inert material. At some point, an ignition zone induced by the previously described compressive wave appears in the region between the inert shock wave and the reactive wave. This ignition point acts as a hot spot, and chemical reactions develop from this point forward and backward in the material, forming two reacting waves. Once again, these reacting waves are preceded by compressive waves. A careful analysis of the diagram reveals that a second hot spot is activated, closer to the front shock. As the reactive wave develops from this point, it catches up with the shock wave, forming a single reactive wave, the overdriven detonation. This overdriven

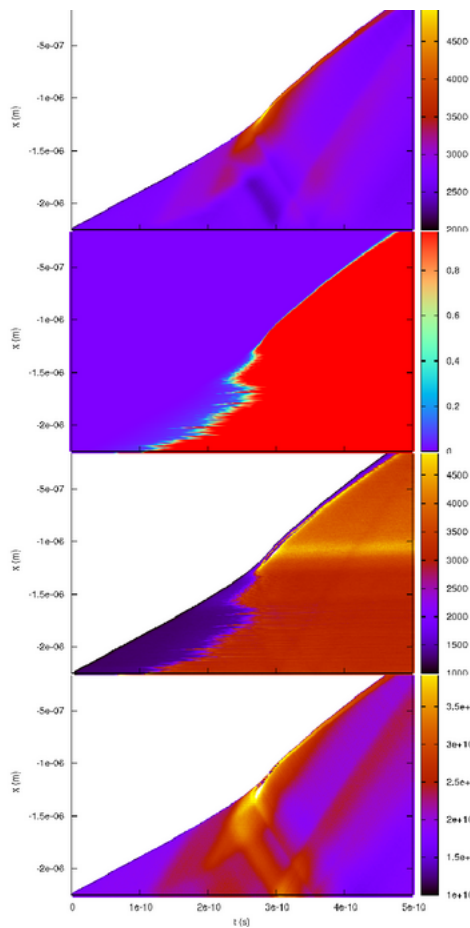


FIG. 3: Coloured maps of thermodynamic variable (particle velocity, progress variable, internal temperature and pressure) in a time-space diagram.

detonation propagates at high speed and is characterized by high particle velocities, as well as high values of thermodynamic variables (temperature, pressure,...). Once formed, the overdriven detonation progressively decays to a stationary detonation, as evidenced in the pressure and temperature diagrams.

In conclusion, we presented for the first time a molecular simulation of a shock-to-detonation transition in a realistic energetic material, using a reduced model based on a DPD coarse graining approach. Our numerical results confirmed the shock to detonation mechanism observed experimentally for nitromethane. Moreover, we have shown that compressive waves are emitted from the onset of chemical reactions, therefore increasing the probability of ignition forward in the material. Hence the reactive wave exhibits a discontinuous progression from sites to sites up to the shock front.

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- [1] J.-B. MAILLET, L. SOULARD, and G. STOLTZ. *Euro. Phys. Lett.*, 78:68001, 2007.
 - [2] B.L. HOLIAN and P.S. LOMDAHL. *Science*, 280:2085, 1998.
 - [3] K. KADAU, T.C. GERMANN, P.S. LOMDAHL, and B.L. HOLIAN. *Science*, 296:1681, 2002.
 - [4] V.V. ZHAKHOVSKII, S.V. ZYBIN, K. NISHIHARA, and S.I. ANISIMOV. *Phys. Rev. Lett.*, 83:1175, 1999.
 - [5] D.W. BRENNER, D.H. ROBERTSON, M.L. ELERT, and C.T. WHITE. *Phys. Rev. Lett.*, 70:2174, 1993.
 - [6] D. HERRING, T.C. GERMANN, and N. GRONBECH-JENSEN. *Phys. Rev. E*, 82:214108, 2010.
 - [7] A. STRACHAN, A.C.T. VAN DUIN, D. CHAKRABORTY, S. DASGUPTA, and W.A. GODDARD. *Phys. Rev. Lett.*, 91(9):098301, 2003.
 - [8] K.I. NOMURA, R.K. KALIA, A. NAKANO, P. VASHISHTA, A.C.T. VAN DUIN, and W.A. GODDARD. *Phys. Rev. Lett.*, 88:148303, 2007.
 - [9] E.J. REED, M.R. MANAA, L.E. FRIED, K.R. GLAESEMAN, and J.D. JOANNOPOULOS. *Nature Physics*, 4:72, 2008.
 - [10] B.L. HOLIAN. *Europhys. Lett.*, 64:330, 2003.
 - [11] A. STRACHAN and B.L. HOLIAN. *Phys. Rev. Lett.*, 94:014301, 2005.
 - [12] G. STOLTZ. *Europhys. Lett.*, 76:849, 2006.
 - [13] K. LYNCH, A. THOMPSON, and A. STRACHAN. *Modelling Simul. Mater. Sci. Eng.*, 17:015007, 2009.
 - [14] Y. KATAOKA. *Bull. Chem. Soc. Jpn.*, 65:2093, 1992.
 - [15] Marsh. *LASL shock hugoniot data*. 1980.
 - [16] P. KLEBERT. *Etude expérimentale et théorique de la transition choc détonation dans les explosifs homogènes*. PhD thesis, Paris VI - Pierre et Marie Curie University, 1998.
 - [17] N. DESBIENS, E. BOURASSEAU, J.-B. MAILLET, and L. SOULARD. *J. of Hazardous Materials*, 166:1120, 2009.
 - [18] V. DUBOIS, N. DESBIENS, and E. AUROUX. *Chem. Phys. Lett.*, 494:306, 2010.
 - [19] R. DAWES, A. SIAVOSH-HAGHIGHI, T.D. SEWELL, and D.L. THOMPSON. *J. Chem. Phys.*, 131:224513, 2009.
 - [20] S.A. SHEFFIELD, D.M. DATTELBAUM, R. ENGELKE, R.R. ALCON, B. CROUZET, D.L. ROBBINS, D.B. STAHL, and R.L. GUSTAVSEN. In proceedings of the 13th Symposium of Detonation, 2006.
 - [21] P. MERCIER, J. BÉNIER, P.A. FRUGIER, M. DEBRUYNE, and B. CROUZET. New models and Hydrocodes for shock wave processes in Condensed Matter, Paris, EPJ web of conference **10**, 00016 (2010), 2010.
 - [22] P. UNGERER, A. BOUTIN, and B. TAVITIAN. *Applications of Molecular Simulation in the Oil and Gas Industry*. IFP Publications, 2005.